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13. ABSTRACT *(Maximum 200 words)*

We have accomplished both tasks stated above and are ready for the next step -building a prototype molecular device based on single molecules. For the first task, we have developed a novel electrochemical technique to fabricate nanoelectrodes separated with an appropriate gap for molecular connection. It starts with a thin metal wire coated with an insulation layer except for a small portion near the center (Fig. Ia), and then etches the center portion electrochemically while monitoring the current through the wire (Fig. lb). As the diameter of the center portion decreases to the electron wavelength (a few A), the conductance becomes quantized and an atomically thin wire is formed. Further etching away the last few atoms produces a pair of nanoelectrodes separated with a small gap, and the ballistic transport responsible for the conductance quantization is replaced by quantum tunneling across the gap (Fig. lc). As we shall show below, the tunneling current is also quantized because of the discrete nature of atoms, which can be used to control the gap width with atomic precision. Once a pair of nanoelectrodes with an appropriate gap is formed, we then bridge the gap with molecules by electrochemical deposition (Fig. ld). In order to quickly fabricate a large array of the nanoelectrodes, we are currently testing a self-terminated method in collaboration with Motorola. We carried out the second task using conducting polymers as a model system. Conducting polymers are attractive electronic materials for a number of reasons.

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Controlling Electron Transfer Through Single Molecules

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Final Report
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OBJECTIVES

The objectives of this project are to seek a better understanding of electron transport in single molecules and to develop a molecular electronic device that can communicate with the outside world in a more practical way than the existing methods. In order to reach the objectives, we will perform the following two tasks:

- Investigate electron transfer through single molecules;
- Fabricate a stable and controllable molecular junction.

STATUS OF EFFORT

We have accomplished both tasks stated above and are ready for the next step – building a prototype molecular device based on single molecules. For the first task, we have developed a novel electrochemical technique to fabricate nanoelectrodes separated with an appropriate gap for molecular connection. It starts with a thin metal wire coated with an insulation layer except for a small portion near the center (Fig. 1a), and then etches the center portion electrochemically while monitoring the current through the wire (Fig. 1b). As the diameter of the center portion decreases to the electron wavelength (a few Å), the conductance becomes quantized and an atomically thin wire is formed. Further etching away the last few atoms produces a pair of nanoelectrodes separated with a small gap, and the ballistic transport responsible for the conductance quantization is replaced by quantum tunneling across the gap (Fig. 1c). As we shall show below, the tunneling current is also quantized because of the discrete nature of atoms, which can be used to control the gap width with atomic precision. Once a pair of nanoelectrodes with an appropriate gap is formed, we then bridge the gap with molecules by electrochemical deposition (Fig. 1d). In order to quickly fabricate a large array of the nanoelectrodes, we are currently testing a self-terminated method in collaboration with Motorola. We carried out the second task using conducting polymers as a model system. Conducting polymers are attractive electronic materials for a number of reasons. First, similar to traditional semiconductors their electrical conductivity can be varied over many orders of magnitude, which can be controlled electrochemically. Second, they are mechanically flexible, which is important

for flexible devices. Finally they are chemically flexible in the sense that many different side branches can be attached to the polymer to tune their electronic and mechanical properties in a tailored fashion. We electrochemically polymerized monomers into polymers and deposited the polymers to bridge the nanoelectrodes fabricated in task 1. One of the most interesting observations is a discrete switching in the conductance of the polymer nanojunction between insulating and conducting states, which may be used as a digital switch controlled by the redox state of the polymer.

We provide below with a summary of the findings.

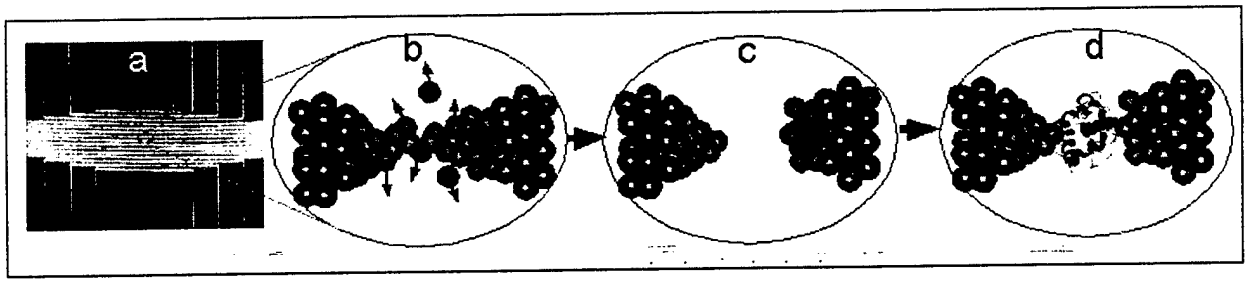


Fig. 1. (a) Microfabricated metal wires on a silicon substrate. (b) When the narrowest portion of the wire is etched down to the atomic scale, its conductance becomes quantized. (c) Further etching away the remaining few atoms, a pair of nanoelectrodes with a small gap is formed and conductance quantization is replaced by quantum tunneling. (d) By bridging the gap with a molecule, one can connect the molecule to the outside world.

ACCOMPLISHMENTS/NEW FINDINGS

Fabrication of stable metallic quantum wire arrays

We have developed a simple method to fabricate stable metallic quantum wires by electrochemically etching a metal wire down to the atomic scale. The conductance of the wire is quantized, given approximately by integer multiples of G_0 ($=2e^2/h$) (Fig. 2). This interesting conductance quantization phenomenon has been observed in semiconductor devices containing a two dimensional electron gas, and in three-dimensional metallic nanowires created mechanically by breaking two electrodes from contact. Because the wavelength of the conduction electrons in metals is of the order of a few Å, one expects that the wire with conductance quantized at the lowest quantum step G_0 be as thin as a single atom. This argument has been recently confirmed by high-resolution transmission electron microscopy that reveals a metallic quantum wire consisting of a string of atoms. We have been able to fabricate an array of the quantum wires with long-term stability (Fig. 2c).

A unique advantage of our method is to fabricate an array of stable quantum wires supported on a solid substrate. In collaboration with Motorola we have demonstrated a 1x15 array of Cu quantum wires supported on an oxidized silicon chip. Using the wires, we have studied chemical sensing possibility based on molecular adsorption-induced conductance changes in the quantum wires.

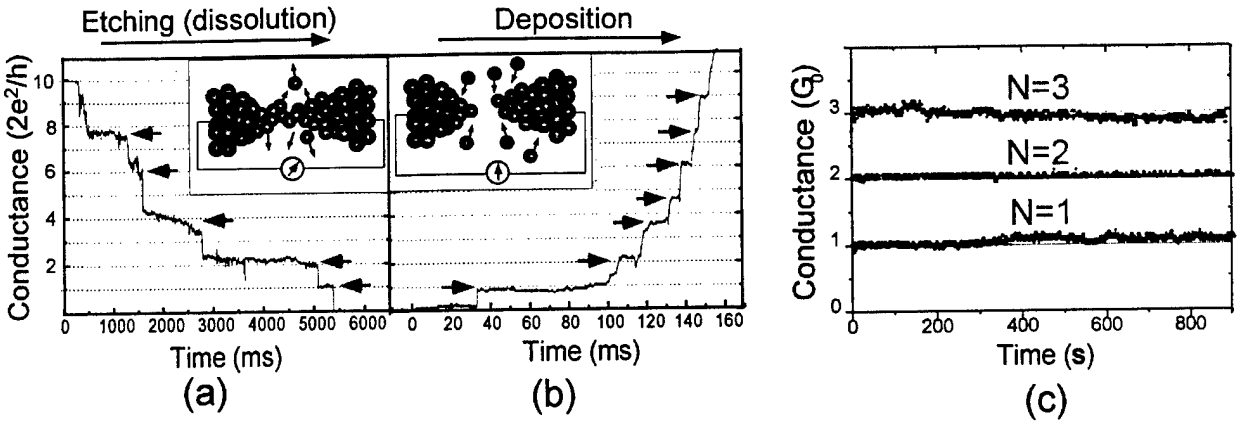
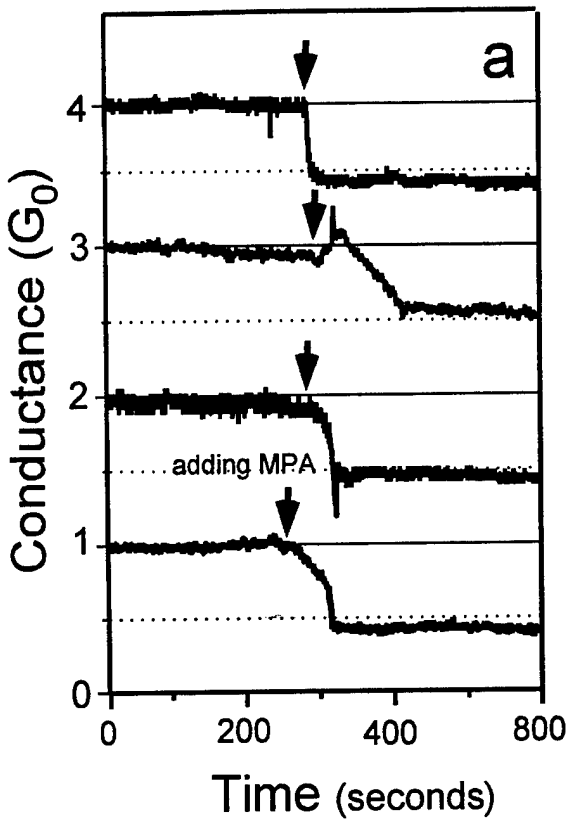


Fig. 2 (a-b) Conductance of a Cu quantum wire during etching (a) and deposition (b). The stepwise change is due to conductance quantization. (c) Stable Cu nanowires with conductance at N=1, 2 and 3 quantum steps.

Molecular detection with metallic quantum wires

We have observed that the conductance of the quantum wires drops abruptly to a fractional value upon molecular adsorption (Fig. 3). The largest drop in conductance occurs in the quantum wires with conductance at the lowest quantum step, and the drop diminishes quickly at higher steps as the quantum ballistic regime is replaced by the classical diffusive regime. The conductance change correlates with the binding strength of the molecules to the metal wires. These observations suggest the possibility of chemical sensor applications based on the adsorbate-induced changes in the quantized conductance of the nanowires, but the mechanism of the conductance change is not understood. One possible mechanism is the scattering of conduction electrons by adsorbates, which reduces the conductance. This theory explains naturally the decreases in the conductance but fails to explain other experimental facts. For example, the mechanical stability of the quantum wires is strongly dependent on molecular adsorption. We have studied the mechanical stability by pulling a quantum wire with a STM and found that the length over which the wire can be elongated before breaking is much longer in the presence of molecular adsorption (Fig. 4). So it is clear that the binding of a molecule onto an atomically thin metal wire affects the mechanical properties of the wire.



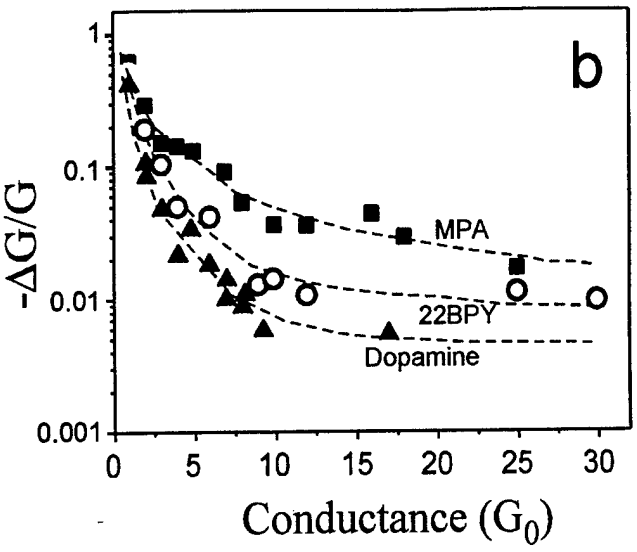


Fig. 3. (a) Conductance change of Cu quantum wires with conductance quantized at 1, 2, 3 and $4G_0$ upon MPA adsorption. (b). Comparison of dopamine-, MPA- and 22BPY-induced conductance changes of Cu nanowire with conductance at various quantum steps.

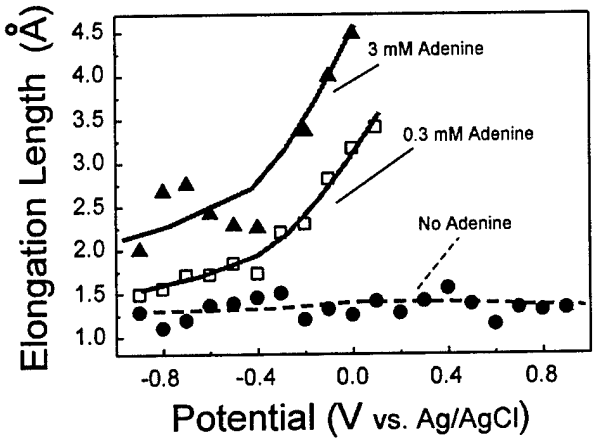


Fig. 4. Elongation length of Au quantum wires with conductance at 1 G_0 as a function of the quantum wire potential in 0.1 M $NaClO_4$, 0.3 mM adenine + 0.1 M $NaClO_4$ and 3 mM adenine + 0.1 M $NaClO_4$. The binding strength increases as the potential.

Fabrication of nanoelectrodes with molecular scale gaps

Starting with a metallic quantum wire, we have created a small gap separating two nanoelectrodes by etching away a few atoms in the narrowest portion of the quantum wire. Consequently, the conductance collapses from the lowest quantum step as ballistic electron transport is replaced by quantum tunneling. The tunneling current also changes in a stepwise fashion (Fig. 5), but the step height is 3-4 orders of magnitude smaller than conductance quantum, $2e^2/h$. Furthermore, the steps in the tunneling current are not equally spaced, instead their heights increase exponentially with the

current (note that logarithmic scale is used in Fig. 5). The stepwise tunneling current is due to the discrete nature of atoms.

Knowing the tunneling current, the width of the gap can be estimated using relation, $I_t \sim \exp(-ks)$, where I_t is the tunneling current, s is the gap width and k is 0.98 ± 0.12 $Å^{-1}$, determined experimentally under a similar condition using a STM setup (inset at upper left corner of Fig. 5a). The corresponding discrete change in the gap width is typically ~ 0.5 Å, which is smaller than the size of an atom, due to atomic reconfiguration. The tendency that the gap stabilizes at discrete steps of ~ 0.5 Å makes it possible to fabricate nanogaps with sub-angstrom precision. Using the procedure we have been able to fabricate molecular scale gaps with a precision of ~ 0.5 Å (Fig. 5, right). The gap width sometimes fluctuates between plateaus with a typical height of ~ 0.5 Å (insets of Fig. 5, right). We attributed the fluctuations to a dynamic equilibrium between deposition and etching that switch the atoms between two stable configurations.

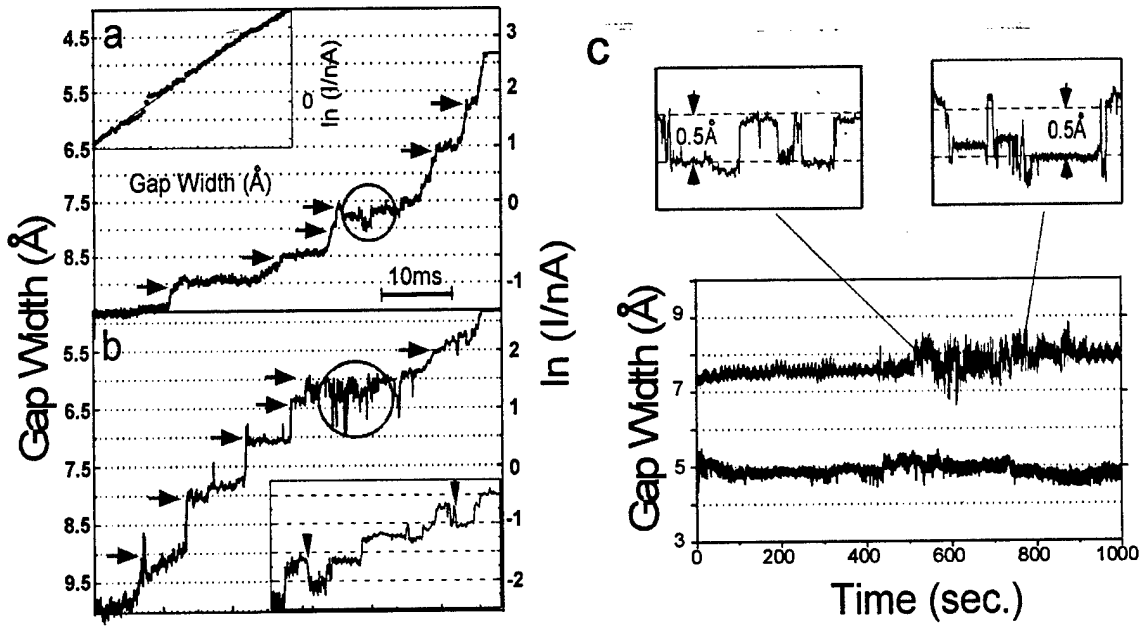


Fig. 5 Left: Tunneling current changes in a stepwise fashion as the gap is widened (narrowed) by electrochemical etching (deposition), due to the discrete nature of atoms. The current often steps down intermittently (inset, lower right corner) and shown as "noise" in the tunneling current (marked by circles). Right: Molecular-scale gap between two electrodes on an oxidized Si can be fabricated and stabilized with a precision of ~ 0.5 Å using the tunneling current as feedback signal. Fluctuations between two stable configurations, corresponding to a gap width change of ~ 0.5 Å, are frequently observed.

Connecting molecules to the nanoelectrodes

By bridging the nanoelectrodes with molecules, we can, therefore, connect the molecules to the external measurement and control units. One example is 1,10'

phenanthroline, a molecule that has two nitrogen atoms ready to bind to transition metals, such as Au and Cu. After connecting the molecule to the nanoelectrodes, we have measured the I-V characteristics, as shown in Fig. 6. The step at ~ -1.5 V and kink at ~ 1.4 V are tentatively attributed to a HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) assisted tunneling. Given the size of the gap it is likely that one or a few molecules dominates the tunneling current, but it is not clear exactly how many molecules bridge the gap.

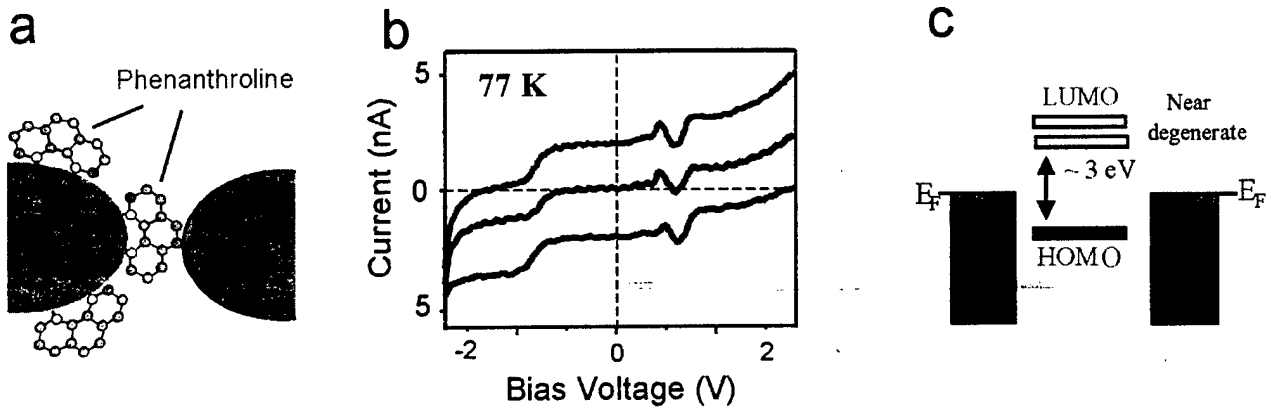


Fig. 6 (a) Schematic of electron transport through phenanthroline between a pair of Au nanoelectrodes fabricated with the electrochemical etching and deposition method. (b) I-V characteristic at 77 K. (c) Schematic of energy diagram of phenanthroline.

We have also investigated electron transport through conducting polymer nanojunction formed between the nanoelectrodes. In sharp contrast to microelectrochemical transistor whose conductance varies smoothly between insulating and conducting states as a function of the electrochemical potential, the polymer nanojunction switches *abruptly* between the insulating and conducting (or off and on) states in a fashion similar to a digital switch (Fig. 7). The nanojunction can switch much faster and with less power than the bulk materials. We have also studied the I-V characteristics of the polyaniline nanowire (Fig. 8). When the "gate" is kept near 0 V (vs. a Ag reference electrode), the I-V curve is linear, similar to that of a metallic wire. Lowering the "gate" below -0.2 V, however, the current vanishes at negative bias sweeps but it increases rapidly at positive bias sweeps. The rectifying characteristic is more pronounced when lowering the "gate" potential to -0.3 V. Our experiment shows that interesting new phenomena occur by reducing the size of the polymer junction.

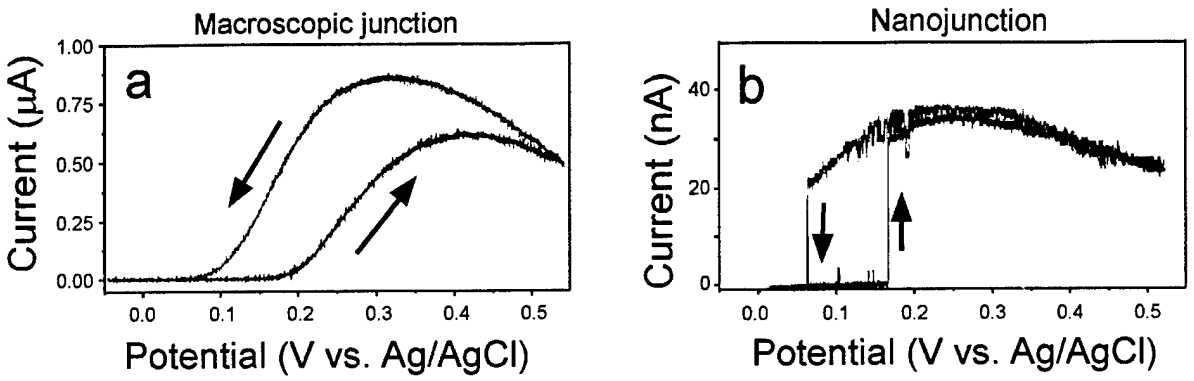


Fig. 7. A polyaniline nanojunction switch. Charge transport current vs. electrochemical potential for polyaniline nanojunctions with two Au nanoelectrodes separated with ~ 50 nm (a) and ~ 1 nm (b). The bias voltage between the nanoelectrodes in each case is 20 mV.

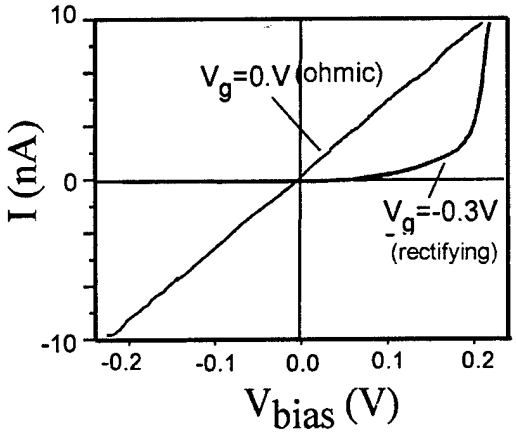


Fig. 8 Partially oxidized polyaniline ("gate" voltage, V_g=0 V) is ohmic. Fully oxidizing or reducing (V_g=-0.3 V) it by controlling the electrochemical potential leads to a rectifying behavior.

PERSONNEL SUPPORTED

- Faculty
  N. Tao (Principal Investigator).

- Post-Docs
  C.Z. Li
  Katie He

- Graduate Students
  Alberto Bogozi
  Osvaldo Lam
  Chen Shu
  S. Hong

- Undergraduate Students
  Sergio Wong
  Joseph Bunch
  John Pean

PUBLICATIONS

Published:

1. C.Z. Li, A. Bogozi, W. Huang and N. J. Tao "Fabrication of Stable Metallic Nanowires with Quantized Conductance", Nanotechnology, 10, 221-223(1999).
2. S. Boussaad and N. J. Tao, "Electron Transfer and Adsorption of Myoglobin on Self-assembled Surfactant Films: An Electrochemical Tapping-Mode AFM Study", J. Am. Chem. Soc., 121, 4510-4515(1999).
3. Q. Jin, J.A. Rodriguez, C.Z. Li, Y. Darici and N.J. Tao, Self-assembly of Aromatic Thiols on Au(111). Surf. Sci., 425, 101-111(1999).
4. C. Shu, C.Z. Li, X. He, A. Bogozi, J. S. Bunch and N.J. Tao, "Fractional Conductance Quantization of Metallic Nanowires under Electrochemical Potential Control", Phys. Rev. Lett., 84, 5196-5199(2000).
5. C.Z. Li, H. X. He, A. Bogozi, J. S. Bunch and N.J. Tao, "Molecular Detection Based on Conductance Quantization of Nanowires", Appl. Phys. Lett., 76, 1333-1336(2000).
6. C. Z. Li, H. X. He, and N. J. Tao, "Quantized tunneling current in the metallic nanogaps formed by electrodeposition and etching", Appl. Phys. Lett., 77, 3995-3997(2000).
7. N.J. Tao, C.Z. Li and H.X. He, "Scanning Tunneling Microscopy Applications in Electrochemistry – Beyond Imaging", invited feature article, J. Electroanal. Chem., 492, 81-93(2000).
8. H. X. He and N.J. Tao, "Conductance of Polymer Nanowires Fabricated by a Combined Electrodeposition and Mechanical Break Junction Method", Appl. Phys. Lett., 78, 811-813(2001).
9. H. X. He, J.S. Zhu, N.J. Tao, L.A. Nagahara, I. Amlani and R. Tsui "A Conducting Polymer Nanojunction Switch", J. Am. Chem. Soc., 123, 7730-7731, 2001.
10. S. Wang, S. Boussaad, and N. J. Tao, "Surface Plasmon Resonance - Enhanced Optical Absorption Spectroscopy for Studying Molecular Adsorbates", Rev. Sci. Instrum., 72, 3055-3060 (2001).
11. A. Bogozi, O. Lam, H. X. He, C.Z. Li, N.J. Tao, L.A. Nagahara, I. Amlani and R. Tsui "Molecular Adsorption onto Metallic Quantum Wires", J. Am. Chem. Soc., 123, 4585-4590(2001).
12. N.J. Tao, "Spectroscopic Applications of SPM in Electrochemistry" in "Encyclopedia of electrochemistry", Volume 2, edited by Bard and Stratmann, Wiely-VCH, in press, 2001.

13. S. Boussaad and N.J. Tao, "Atom-Size Contacts and Gaps Between Electrodes Fabricated with a Self-Terminated Electrochemical Method", Appl. Phys. Lett., 80, 2398-2400, 2002.
14. H.X. He, S. Boussaad, B. Xu, S. Bousssaad and N. J. Tao "Electrochemical Fabrication of Nanowires and Nanogaps", J. Electroanal. Chem., 522, 167-172, 2002.
15. H. X. He and N. J. Tao "Interaction of Molecules with Metallic Quantum Wires", Adv. Mat., 14, 161-164, 2002.
16. H. X. He, C. Shu, C. Z. Li and N. J. Tao, "Adsorbate Effect on the Mechanical Stability of Atomically Thin Metallic Wires", J. Electroanal. Chem., 522, 26-32, 2002.

INTERACTIONS/TRANSITIONS

Participation/Presentations At Meetings, Conferences, Seminars, Etc

INVITED TALKS:

1. 195th Electrochemical Society Meeting, invited talk, May, 1999.
2. Washington State University, Colloquium, Sept., 1999.
3. Georgia Institute of Technology, Physics Colloquium, Atlanta, December, 1999.
4. 26the Annual Conference of Federation of Analytical Spectroscopy, Vancouver, Oct., 1999.
5. North Carolina State University, seminar, Nov., 2000.
6. 197th American Electrochemical Society Meetings, Symposium on Scanning Tunneling Microscopy, Oct., Phoenix, 2000.
7. Quantum Electronics Labs, Motorola, June, 2000.
8. Molecular Electronics Symposium, Phoenix, May, 2000.
9. 196th American Electrochemical Society Meetings, Toronto, May, 2000.
10. Biomolecular Application of Scanning Probe Microscopy –2000 Workshop, The Royal Danish Academy of Sciences and Letters, Copenhagen, March, 2000.
11. American Vacuum Society, Southeast chapter, annual conference, Orlando, March, 2000.
12. Institute of Solid State Science, Chinese Academy of Science, Dec. 2001.
13. Anhui University, China, seminar, Dec. 2001.
14. University of Heidelberg, Germany, Seminar, Dec. 2001.
15. University of Karlsruche, Germany, Seminar, Dec., 2001.
16. Workshop on Electrochemical Fabrication of Nanostructures, Reisenberg, Germany, Nov., 2001.
17. 199th Electrochemical Society Meetings, San Francisco, September, 2001.
18. American Chemical Society, Chicago, August 26, 2001.
19. 9th International Conference on Electrified Interfaces, Wolfville, July, 2001.
20. 84st Canadian Chemical Society Conference, Montreal, May, 2001.

21. University of Miami, seminar, April 20, 2001.
22. Florida Atlantic University, seminar, January 19, 2001.
23. Gordon Research Conference, Ventura Beach, CA, Jan. 21, 2002.
24. CSSER, Arizona State University, March 22, 2002.
25. Purdue University, seminar, "Connecting Single Molecules to Nanoelectrodes", May 9, 2002.
26. 200th Electrochemical Society Meetings, May 13, 2002.

CONTRIBUTED TALKS:

1. 199th Electrochemical Society Meetings, San Francisco (2 papers), September, 2001.
2. International Nanomaterials Conference, Atlanta, Georgia (2 papers), October, 2000.
3. American Chemical Society, Washington (2 papers), August, 2000.
4. 196th ECS meetings, May, Toronto, 2000.
5. American Chemical Society, New Orleans, August, 1999.
6. American Electrochemical Society, Seattle, May, 1999.
7. American Physical Society, Atlanta, March, 1999.

NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES

N.J. Tao, S. Boussaad and W.L. Huang, "High Resolution Surface Plasmon Spectroscopy", International Patent #WO0070328, 2001.

N.J. Tao and S. Boussaad "An Automated Method to Fabricate Arrays of Atomic-Scale Contacts and Molecular-Scale Gaps between Electrodes", U.S. Provisional Patent, 2001.

TECHNOLOGY TRANSFER

The quantum electronics lab of Motorola has been using the technique developed in this project to fabricated nanoelectrodes for molecular electronics applications. Semiconductor Research Corporation has provided a $35,000 to further develop the techniques to fabricated single molecular junctions.